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(54) Title: LOW MONOMER FOAM

(57) Abstract: A process for producing a two component polyurethane foam, which process comprises mixing (A) a polyol resin component; (B) an isocyanate component having a free monomeric diisocyanate content of not more than 2 % by weight; and (C) a catalyst blend comprising at least two catalytic materials selected from (a) organometallic catalysts, (b) amines and (c) isocyanurate catalysts.

LOW MONOMER FOAM

The present invention relates to processes for producing two component polyurethane foams utilising an isocyanate component with a reduced level of
5 monomeric diisocyanate.

Two component foams are well known and are produced by the reaction of an isocyanate component and a polyol component. There are many other ingredients required to produce finished foam, for example blowing agents, cell stabilisers and catalysts.

10 Two component foams are used in a variety of applications as sound and/or vibration absorbers or dampers and as thermal insulation including in automotive assembly, white consumer goods, insulation panels, refrigeration units, void fillers and tank insulation. High levels of monomeric isocyanates are normally required to be present to produce a polyurethane foam with useful properties and sufficient
15 mechanical strength. The curing process of such foams is an exothermic reaction, and this rise in temperature can also assist the evaporation of monomeric isocyanate. However a problem is currently encountered in applications where the material is applied in a poorly ventilated area or is "foamed-in-place". This is due to the adverse health effect of exposure to isocyanates, which is well known and a recognised
20 concern within the industry.

Therefore there is currently difficulty in many situations where it is not possible to put in place adequate ventilation and control measures. In such cases use of conventional two component foams is usually avoided.

The present invention overcomes the above problems by providing a process
25 for producing a useable foam from two component compositions wherein the harmful monomeric diisocyanate component has been removed at source. The monomeric diisocyanate content has previously been considered to be a necessary component to produce desirable properties such as high reactivity and rapid gelling. However, surprisingly, a useable foam can be produced using an isocyanate component with a
30 reduced free diisocyanate level. This has been achieved through addition of a catalyst blend to the reaction mixture.

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The present invention therefore provides a process for producing a two component polyurethane foam which comprises mixing

- (A) a polyol resin component;
- (B) an isocyanate component having a free monomeric diisocyanate content of not more than 2% by weight; and
- (C) a catalyst blend, suitably comprising at least two different catalyst materials, each selected from (a) organometallic catalysts, (b) amines and (c) isocyanurate catalysts.

In a preferred embodiment of the invention a component comprising the polyol resin component (A) and the catalyst blend (C) is mixed with the isocyanate component (B).

Conventional additives may be incorporated into the foam as is customary in the art. Optionally such additives include fillers which modify foam density and/or improve vibration damping and sound insulation properties. Reinforcing fillers which do not react with the isocyanate component, such as glass and plastic fibres, talc and other non-reactive inorganic fillers, may be used for this purpose.

The catalyst blend (C) usually includes catalyst materials from each of two of the three classes (a) organometallic catalysts, (b) amines and (c) isocyanurate catalysts and preferably contains at least one member of each of these three classes. However since some catalytic species may fall into two classes simultaneously and since the classes are therefore not completely mutually exclusive it is possible to contemplate the use of only two different catalysts, both falling into the same class.

Organometallic catalysts which may be utilised in the present invention include dibutyltin dilaurate, lead naphthanate, cobalt naphthanate, dibutyltin dilauryl mercaptan, dibutyltin bis(isooctyl maleate), dibutyltin bis (methyl maleate), dibutyltin bis(isooctyl thioglycollate) and dibutyltin diacetate. Such catalysts when present are used in an amount of from 5 to 50% by weight of the catalyst blend.

Examples of the amine catalysts which can be used are tri(3-dimethylaminopropyl)amine, N,N,N',N'',N'''-pentamethyldiethylenetriamine, bis(dimethylamino) ethyl ether, dimethylcyclohexylamine, N,N,N',N'''-tetramethylethylenediamine, dimethylethanolamine, 2-(2-dimethylamino ethoxy)-

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ethanol and triethylene diamine. These compounds when present are used in an amount of from 5 to 85%, for instance 5 to 50 % by weight of the catalyst blend.

As used herein the term "isocyanurate catalyst" refers to materials which promote the formation of isocyanurate groups from any isocyanate that they come into contact with. Isocyanurate catalysts suitable for use in the present invention include N, N', N''- tris (3-dimethylaminopropyl) hexahydro-s-triazine, bis-(3-dimethylaminopropyl) isopropanolamine, n-(2-hydroxypropyl)-n-trimethylammonium formate and other quaternary ammonium salts, and metal salts including sodium and potassium compounds such as potassium acetate and potassium and stannous octoates. In particular, Baxcat 0, a proprietary isocyanurate catalyst supplied by Baxenden Chemicals Ltd., may be used. Such compounds when present are used in an amount of from 5 to 75 % by weight of the catalyst blend.

The catalyst blend may optionally comprise other additives, for example triethylene glycol diamine.

It is desirable for the catalyst blend to be present in a range of from 0.1 to 20%, for instance 5 to 20%, preferably 7 to 15 %, of the total weight of components (A) and (C).

The polyols of component (A) are typically hydroxyl terminated compounds with molecular weight of approximately 200 to 10000, with a hydroxyl functionality ranging from 2 to 6. Typical examples of suitable polyols are hydroxyl terminated polyoxypropylene polyols, polyesters, polycaprolactones, polyoxyethylene polyols, polytetramethylene glycols, copolymers of polyoxypropylene-polyoxyethylene polyols and Mannich bases. A formulation of component (A) may, for example, consist of 40 to 60 % polyoxypropylene triols, 15 to 35 % polyoxypropylene diols, 8 to 12 % diethanolamine, with additives such as silicones and water.

It is preferred that the isocyanate of component (B) has a free monomeric diisocyanate component of not more than 0.5% by weight.

The isocyanate component (B) can be aromatic, aliphatic, cycloaliphatic or heterocyclic materials prepared by producing dimers, trimers, oligomers or prepolymers from monomeric diisocyanate or polyisocyanate followed by a distillation process to remove any residual free monomer to less than 2.0%,

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preferably 0.5%, by weight. Such di- or polyisocyanate materials may be produced conventionally from, for example, ethylene diisocyanate, propylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, 2,4,4-trimethylhexamethylene-1,6 diisocyanate, phenylene diisocyanate, toluene or naphthylene diisocyanate, 4,4'-methylene-bis (phenyl isocyanate); 4,4'-ethylene-bis (phenyl isocyanate), ω,ω' -diisocyanato-1,3-dimethyl benzene, ω,ω' -diisocyanato-1,4-dimethyl cyclohexane, ω,ω' -diisocyanato-1,4-dimethyl benzene, ω,ω' -diisocyanato-1,3-dimethylcyclohexane, 1-methyl-2,4-diisocyanatocyclohexane, 4,4'-methylene-bis (cyclohexyl isocyanate), 3-isocyanato-methyl-3,5,5-trimethyl cyclohexyl isocyanate, dimer acid-diisocyanate, ω,ω' -diisocyanato-diethyl benzene, ω,ω' -diisocyanatodimethyl toluene, ω,ω' -diisocyanato-diethyl toluene, fumaric acid-bis (2-isocyanato ethyl) ester or triphenyl-methane-triisocyanate, 1,4-bis(2-isocyanato-prop-2-yl)benzene, or 1,3-bis(2-isocyanato prop-2-yl)benzene. Such di- or polyisocyanate materials may have a biuret or allophanate structure or may be isocyanurates. Polyisocyanate prepolymers may be obtained by reaction of for instance an excess amount of the isocyanate with a dihydric reagent such as (i) water, (ii) a lower molecular weight polyol (molecular weight not greater than 300) or (iii) a medium molecular weight polyol (molecular weight greater than 300 and less than 10000).

The polyols of component (B) are typically hydroxyl terminated compounds with molecular weight of approximately 200 to 10000, with a hydroxyl functionality ranging from 2 to 6. Typical examples of suitable polyols are hydroxyl terminated polyoxypropylene polyols, polyesters, polycaprolactones, polyoxyethylene polyols, polytetramethylene glycols and copolymers of polyoxypropylene-polyoxyethylene polyols.

The distillation process may be carried out by any suitable conventional distillation technique appropriate for the reactivity of the isocyanates, such as wiped film distillation under reduced pressure.

Certain low residual monomer isocyanates are commercially available, for example a hexamethylene diisocyanate biuret, which can be utilised as the isocyanate

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component of the foam.

The components can be mixed and applied through equipment known in the art for use in the production of foams. In the case of two component foams, commercially available plural component polyurethane mixing and metering equipment may be used. For example a low output, high pressure machine equipped with a third component metering pump may be used, enabling a blowing agent to be accurately added to one of the streams, at a rate of up to 6% by volume. An example of such equipment is a positive displacement metering machine fitted with an impingement mixing head.

The mixtures obtained by a process according to the present invention have high reactivity and rapid gelling times and thus produce satisfactory polyurethane foams despite the use of an isocyanate component having low levels of monomeric diisocyanate. In particular, they conveniently, but not essentially, conform to the following specification:

15

Reactivity specification (Cup test at 20°C)

Cream time = 1 to 75 seconds, for instance 1 to 20 seconds

Gel time = 5 to 210 seconds, for instance 5 to 40 seconds

Rise time = 10 to 360 seconds, for instance 10 to 50 seconds

20 Free rise density = 10 to 600 kg.m⁻³, for instance 35 to 500 kg.m⁻³

The present invention is illustrated further by means of the following Examples:

25 Example 1

Product formulation

(A) Polyol resin component and (C) Catalyst blend

30

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	Constituent	%
	Polyoxypropylated glycerol OH _v = 56	26.5
5	Polyoxypropylated glycerol OH _v = 36	26.5
	Polyoxypropylated toluene diamine OH _v = 415	15.0
	Polyoxypropylene diol OH _v = 280	10.5
10	Diethanolamine	10.0
	B 8404 (Goldschmidt Ltd) (Polyether modified polysilicone)	1.0
	Water	0.5
	Triethylene glycol diamine	2.0
15	Dibutyltin dilaurate	1.5
	Baxcat 0 (Baxenden Chemicals Ltd.)	4.5
	Tri(3-dimethylaminopropyl)amine	2.0

Resin viscosity @ 20°C = 980 cps (Brookfield-Spindle 3, speed 60 rpm)

20 SG @ 20°C = 1.038

All ingredients are hand mixed to a homogenous solution at 20°C.

OH_v = hydroxyl value

(B) Isocyanate component

25	Constituent	%
	Hexamethylene diisocyanate biuret	90
	Propylene carbonate	10

% NCO = 20.7

30 Viscosity @ 20°C = 1010 cps (Brookfield-Spindle 3, speed 60 rpm)

SG @ 20°C = 1.126

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Both ingredients are hand mixed to a homogenous solution at 20°C.

Mix ratio resin:isocyanate = 45:55 by weight
47:53 by volume.

5

Laboratory mixing of the isocyanate and resin component is carried out at 20°C using an electric drill fitted with a circular agitator. at a rotational speed of 3000 rpm.

Results for lab mix @ 20°C

10 Mix size = 200 g
Mix time = 5 s

Product specification

% NCO = $20.7 \pm 0.5\%$

15 Isocyanate viscosity @ 20°C = 900 to 1100 cps (Brookfield-Spindle 3, 60 rpm)
Resin viscosity @ 20°C = 900 to 1100 cps (Brookfield-Spindle 3, 60 rpm)

Approximate reactivity (Cup test @ 20°C)

Cream = 5 to 7 s

20 Gel = 11 to 14 s

Rise = 21 to 26 s

Density = 135 to 165 kg.m⁻³

Example 2

25

The formulation of (A), (B) and (C) of Example 1 was dispensed through a mixing machine with tetrafluoroethane (4% by weight) being added via the machine to act as a cell control agent for the foam.

30 Machine settings

Chemical temperature = 70°C (150°F)

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Mixing pressure = 1000 psi

Cream time = Immediate

Gel time = 3 s

5 Foam propertiesCore density = 100 to 120 kg/m³

Closed cell content (ASTM D2856) = 3.6%

Flammability test, MVSS 302 (burn rate) = 3.05 cm/min (1.2 inches/min)

10 Dimensional stability (ASTM D2126):

Conditions	% change in dimension			
	Length	Breadth	Thickness	Volume
24 hrs @ 100°C	-2.18	-1.90	-0.36	-4.39
24 hrs @ -15°C	-0.33	-0.27	+0.2	-0.41

15

Examples 3 to 9 were carried out in accordance with the process described in Example 1 and using the component formulations specified below:

Example 3:

20

(A) polyol component and (C) catalyst blend.

Constituent	%
25 Polyoxypropylated glycerol OHv = 36	26.3
Polyoxypropylene diol OH _v = 280	10.5
Water	0.8
30 B8404 (Goldschmidt Ltd.) (Polyether modified polysilicone)	1.0
Triethylene glycol diamine	2.0

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	Tris(3-dimethylaminopropyl)amine	2.0
	Dibutyltin dilaurate	1.5
	Polyoxypropylated glycerol OHv = 56	26.5
5	Polyoxypropylated toluene diamine OHv = 415	15.0
	Baxcat O (Baxenden Chemicals Ltd.)	5.5
	Diethanolamine	8.9

10

(B) Isocyanate component

	Constituent	%
15	Hexamethylene diisocyanate isocyanurate ($< 0.3\%$ free monomer)	90.0
	Triethylphosphate	10.0

% NCO = 19.7

20 Mix ratio, resin : isocyanate = 45 : 55 by weight

Mix time = 5 secs

Mix size = 100 g

Approximate reactivity (cup test @ 20°C)

25

Cream = 6 to 10 s

Gel = 20 to 28 s

Density = 135 to 165 kgm⁻³

30

Example 4:

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(A) polyol component and (C) catalyst blend.

	Constituent	%
5	Mannich base OHv = 620	30.0
	Polyoxypropylated glycerol OHv = 56	51.7
	Triethylphosphate	10.0
	Water	0.8
10	Triethylene glycol diamine	2.0
	N,N,N',N'',N''' - pentamethyldiethylenetriamine	2.0
	Dibutyltin dilaurate	1.0
	B8871 (Goldschmidt Ltd.) (Polyether modified polysilicone)	1.5
15	B8934 (Goldschmidt Ltd.) (Polyether modified polysilicone)	1.0

(B) Isocyanate component

20

	Constituent	%
	Hexamethylene diisocyanate uretdione ($< 0.5\%$ free monomer)	55.0
25	Castomer E1004 (Baxenden Chemicals Ltd) TDI prepolymer ($< 0.1\%$ free monomer)	35.0
	Triethylphosphate	10.0

30 % NCO = 15.25